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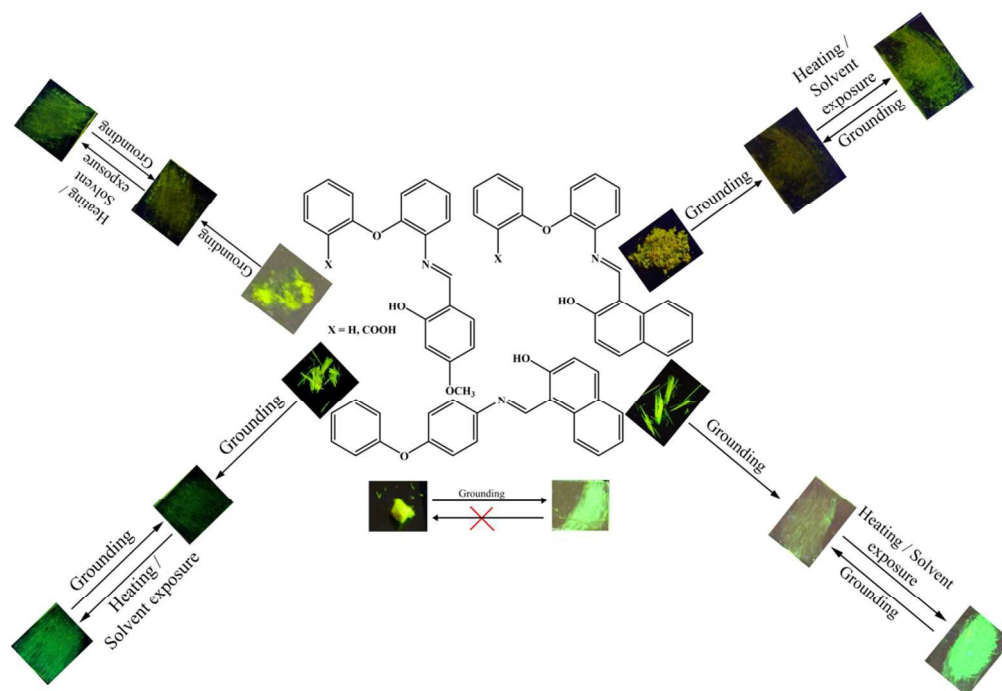
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Stimuli responsive reversible high contrast off-on fluorescence switching of simple aryl-ether amine based aggregation induced enhanced emission materials

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Stimuli responsive reversible high contrast off-on fluorescence switching of simple aryl-ether amine based aggregation induced enhanced emission materials

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DOI: 10.1039/b000000x

Aryl-ether amine based simple Schiff base molecules (1-5) showed aggregation induced enhanced emission (AIEE) in the solid state and rare stimuli responsive fluorescence off-on switching. Hard grounding of 1 showed irreversible fluorescence tuning from greenish-yellow to green. Heating or solvent exposure did not show any reversibility of the fluorescence. Interestingly, hard grounding of 2-5 lead to the quenching of solid state fluorescence and heating/solvent exposure produced clear bright fluorescence. Importantly, 2-5 exhibited reversible off-on fluorescence switching for several cycles without significant change of fluorescence intensity. It is noted that the turn-on fluorescence of 2-5 was slightly blue shifted compared to the initial solids. PXRD studies suggest that the switching of dark to bright fluorescence and vice versa of 2-5 is due to the reversible change of crystalline to amorphous phase and more planarization of twisted structure. Single crystal analysis of 1 and 5 confirmed the twisted molecular conformation and strong intermolecular interactions in the crystal lattice that lead to AIEE by restricting the free rotation and rigidifying the fluorophores in the solid state. The high contrast dark and bright fluorescence switching of 2-5 could be of potential interest in optoelectronic applications.

20 Introduction

Developing stimuli responsive organic fluorescent materials particularly with repeated fluorescence switching has received considerable interest because of their potential applications in sensors, displays, switches, security inks, optoelectronic devices, and data storage.^{1,2} In general, switching of organic solid state fluorescence have often been achieved either by altering the fluorophore packing and conformation or controlling the intermolecular interactions in the solid state structures.³⁻⁵ The external stimuli such as mechanical force, heat and solvent exposure often changes the molecular conformation or phase of the materials (crystalline to amorphous) and lead to switching of solid state fluorescence. Organic molecules that exhibit temperature dependent molecular packing in crystals showed highly reversible fluorescence switching.⁶ The inclusion and removal of guest molecules in the crystal lattices of supramolecular organic fluorescent host materials lead to fluorescence switching.⁵ In recent years, aggregation induced enhanced emission (AIEE) phenomenon, weakly or non-emissive fluorophores in solution but strong emission in the aggregated state, has been successfully used for developing efficient solid state fluorescent materials.⁷ The rigidification of fluorophores in the aggregated state restrict the intramolecular rotation and activate the radiative decays. Some of the strongly fluorescent AEE materials exhibited external stimuli responsive fluorescence

switching due to the change of fluorophore conformation or phase of the materials.^{8,9} For example, conformationally twisted tetraphenylpyrene, pyrene- and anthracene-based liquid crystals, cyanostilbene and triphenylamine derivatives exhibited reversible fluorescence switching with external force.¹⁰ Most of these materials showed only the color transformation with external force rather than the change of fluorescence efficiency that hamper the materials to be used for high-contrast fluorescence recording.

Park's et al. reported the unique example of high contrast reversible fluorescence on-off by external force using dicyanodistyrylbenzene based donor-acceptor-donor triad.¹¹ Solvent inclusion/removal in coordination complexes showed dramatic fluorescence changes in intensity.¹² However, the examples of fluorescent material that exhibit external stimuli such as heat, pressure and vapor responsive fluorescence on-off switching with high contrast are rarely reported compared to change of color.^{6a,13,14} The integration of anthracene unit with AEE active diphenylquinoxaline core lead to heat responsive fluorescence on-off in the solid state.¹⁵ Zhang et al recently reported heating and mechanical force induced fluorescence on-off in a triphenylamine based fluorophore.¹⁶ In our effort to develop new organic solid state fluorescence switching materials,¹⁷ we report here the synthesis of aryl-ether amine based Schiff base molecules that exhibit AIEE in the solid state and stimuli responsive reversible fluorescence off-on switching (Scheme-1). Schiff bases were chosen in view of their facile

synthesis and good photophysical properties that found applications in many research fields such as chemicals molecular optoelectronics, photochromism and medicine.¹⁸ The greenish-yellow fluorescence of 1 in the solid state was tuned to green by hard grounding. 1 did not show any fluorescence switching. However, 2-5 exhibited clear off-on fluorescence switching and showed reversible dark and bright fluorescence with external force. The greenish-yellow or yellow fluorescence of 2-5 was quenched by hard grounding and heating or solvent exposure turn-on the fluorescence. The turn-on fluorescence of 2-5 after the external stimuli (grounding/heat/solvent vapor) was slightly blue shifted compared to initial solids. Importantly, the fluorescence off-on switching of 2-5 could be reproduced for several cycles by repeated grounding and heating. PXRD studies suggest that fluorescence on-off switching could be attributed to the reversible change of crystalline to amorphous phase. Single crystal analysis of 1 and 5 showed twisted molecular conformation and strong intermolecular interactions in the crystal lattice that rigidify the fluorophores and induced AIEE. Thus simple Schiff base organic molecules showed rare high contrast stimuli responsive fluorescence off-on switching in the solid state that could be of interest in optoelectronic device studies.

Materials and methods

2-fluoro-nitrobenzene, 4-fluoro-nitrobenzene, phenol, 2-cyanophenol, NaBH₄, Pd/C, 2-hydroxy naphthaldehyde and 2-hydroxy-4-methoxy benzaldehyde was obtained from sigma-Aldrich and used as received. The solvents were obtained from Merck India. All chemicals are used as received. The aryl-ether amine precursors and Schiff base molecules (1-5) were synthesized by following our recently reported procedure (Scheme S1).¹⁹ The melting points of the compounds were obtained from DSC spectra (Fig. S1)

Synthesis of 1-3

1 was synthesized by adding ethanol (20 ml) dissolved 2-hydroxy-4-methoxy benzaldehyde (1.1mmol) into stirring solution of 2-aminophenoxybenzene (1mmol) in ethanol (5 ml) drop-wise under ambient condition. The resultant reaction mixture was refluxed for 4 h. The product was precipitated out upon cooling the reaction mixture to room temperature. The precipitate was filtered, washed with ethanol and dried under vacuum. 2 has been synthesized in a similar procedure but by using 2-hydroxy naphthaldehyde (1.1mmol) in ethanol whereas 3 was prepared using 4-aminophenoxybenzene (1mmol) and 2-hydroxy naphthaldehyde (1.1mmol) in ethanol.

1: Yield = 85 %. m.p. 117.2 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 13.54 (s, 1H), 8.57 (s, 1H), 7.32 - 7.27 (m, 3H), 7.23 - 7.19 (m, 3H), 7.07 - 7.05 (m, 2H), 6.98 - 6.95 (m, 2H), 6.45 - 6.42 (dd, *J* = 1.2, 2.0 Hz, 2H), 3.80 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 164.5, 164.2, 162.0, 157.8, 149.3, 140.4, 133.6, 129.8, 127.4, 124.9, 122.9, 121.3, 120.4, 117.6, 113.3, 107.2, 101.2, 55.5. *m/z* Calcd. for C₂₀H₁₇NO₃ (M+H): 319.12, found: 320.1.

2: Yield = 90 %. m.p. 163.2 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 15.40 (s, 1H), 9.32 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 9.2 Hz, 1H), 7.63 (d, *J* = 8 Hz, 1H), 7.49 - 7.45 (m, 2H), 7.36 - 7.25 (m, 3H), 7.23 - 7.19 (m, 2H), 7.12 - 7.02 (m,

4H), 6.96 (d, *J* = 9.2 Hz, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 173.1, 157.0, 153.1, 148.8, 137.4, 135.8, 133.5, 129.9, 129.5, 128.2, 127.2, 127.0, 124.5, 123.6, 123.6, 123.4, 120.1, 119.0, 118.8, 118.6, 108.9. *m/z* Calcd. for C₂₃H₁₇NO₂ (M+H): 339.13, found: 340.1.

3: Yield = 82 %. m.p. 132.6 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 15.53 (s, 1H), 9.33 (s, 1H), 8.09 (dd, *J* = 4 Hz, 1H), 7.78 (dd, *J* = 4.4 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.39 - 7.32 (m, 5H), 7.16 - 7.04 (m, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 168.8, 157.0, 156.0, 154.8, 141.1, 136.2, 133.1, 129.9, 129.3, 128.0, 127.4, 123.5, 123.5, 121.8, 119.8, 118.9, 108.9. *m/z* Calcd. for C₂₃H₁₇NO₂ (M+H): 339.13, found: 340.1.

70 Synthesis of 4 and 5

Ethanol solution (30 ml) of aldehyde (1.1mmol, 2-hydroxy-4-methoxy benzaldehyde (4), 2-hydroxy naphthaldehyde (5)) was added drop-wise into 2-(2'-aminophenoxy)benzene carboxylic acid (1mmol) dissolved in ethanol (10 ml) under stirring at room temperature. After the addition, the reaction mixture was refluxed for 10 h. The cooling of reaction mixture produced precipitate that was filtered and washed with ethanol and dried under vacuum.

4: Yield = 85 %. m.p. 158.8 °C. ¹H NMR (300 MHz, d₆-DMSO) δ 13.50 (s, 1H), 12.84 (s, 1H), 8.91 (s, 1H), 7.83 (dd, *J* = 1.8 Hz, 1H), 7.57 - 7.54 (m, 2H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.28 - 7.25 (m, 3H), 6.97 - 6.94 (m, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.49 (dd, *J* = 2.7, 2.4 Hz, 1H), 6.37 (d, *J* = 2.4 Hz, 1H), 3.77 (s, 3H). ¹³C NMR (75 MHz, d₆-DMSO) δ 166.2, 163.6, 163.4, 162.6, 155.8, 149.0, 138.9, 134.0, 133.4, 131.5, 124.7, 122.9, 120.0, 119.7, 118.3, 112.8, 106.6, 100.6, 55.3. *m/z* Calcd. for C₂₁H₁₇NO₅ (M+H): 363.11, found: 364.1.

5: Yield = 86 %. m.p. 224 °C. ¹H NMR (300 MHz, d₆-DMSO) δ 15.79 (s, 1H), 12.98 (s, 1H), 9.68 (s, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 8.08 - 8.05 (dd, *J* = 3.1 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 9.3 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.61 - 7.53 (m, 2H), 7.34 - 7.22 (m, 4H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.86 - 6.78 (m, 2H). ¹³C NMR (300 MHz, d₆-DMSO) δ 173.4, 166.0, 154.7, 153.1, 148.9, 137.4, 133.7, 133.3, 131.7, 128.9, 128.0, 127.0, 126.2, 124.2, 123.8, 123.7, 123.3, 123.2, 120.9, 120.0, 119.0, 117.3, 108.3. *m/z* Calcd. for C₂₄H₁₇NO₄ (M+H): 383.12, found: 384.1.

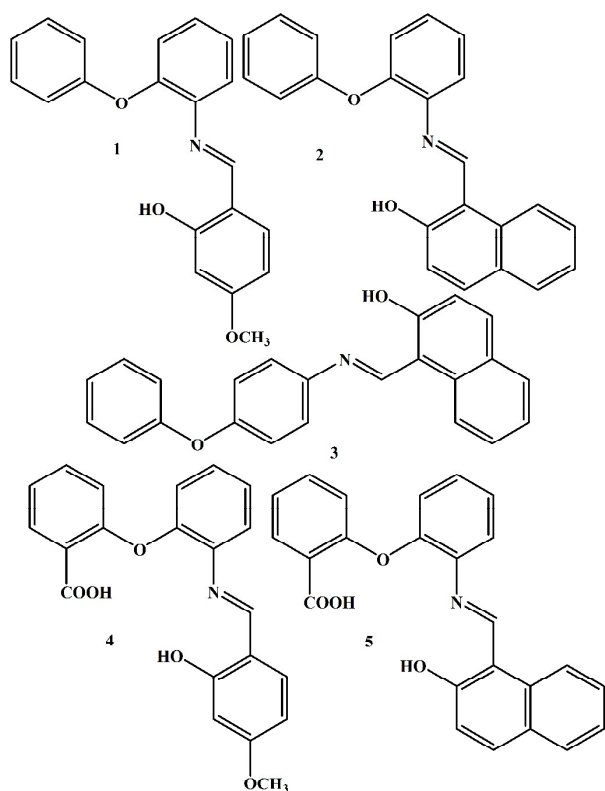
Spectroscopy and structural characterization:

Absorption and fluorescence spectra were recorded using Perkin Elmer Lambda 1050 and Jasco fluorescence spectrometer-FP-8200 instruments. Fluorescence quantum yields (Φ_f) of solid samples were measured using a Horiba Jobin Yvon model FL3-22 Fluorolog spectrofluorimeter with integrating sphere. The powder X-ray diffraction (PXRD) patterns were measured using a Bruker D8 Advance XRD with Cu Kα radiation (λ = 1.54050 Å) operated in the 2θ range from 10° to 50°. Single crystal of 1 and 5 was coated with paratone-*N* oil and the diffraction data measured at 100K with synchrotron radiation (λ = 0.62998 Å) on a ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. CCDC-1418264 (1), 1417738 (5) contains the supplementary crystallographic data for this paper.

Spectroscopy and characterization: Absorption and fluorescence spectra were recorded using Perking Elmer Lambda 1050 and Jasco fluorescence spectrometer-FP-8200 instruments. IR spectra were recorded using KBr disks on a Shimadzu affinity spectrophotometer over the range 4000 - 400 cm^{-1} using KBr as the reference.

Result and Discussion

The synthesis of amine precursors and the corresponding Schiff base molecules (1-5) are shown in scheme S1. The reaction between phenol and 2-fluoro-nitrobenzene or 4-fluoro-nitrobenzene in presence of K_2CO_3 in DMSO at 110 $^\circ\text{C}$ yielded the corresponding aryl-ether with nitro group at *ortho* or *para* position. The subsequent nitro group reduction produced amine precursors for 1-3. The reaction between 2-cyanophenol and 2-fluoro-nitrobenzene in presence of K_2CO_3 in DMSO at 110 $^\circ\text{C}$ resulted in the formation of 2-(2-nitrophenoxy)benzotrile. The nitro group reduction followed by oxidation of CN to COOH produced amine precursor for 4 and 5. The Schiff base molecules (1-5) were synthesized using a simple condensation reaction between the amine and aromatic aldehydes in ethanol. The synthesized Schiff base compounds (1-5) showed greenish-yellow to yellow fluorescence in the solid state. However, 1-5 did not show any fluorescence in solution state that could be due to the free rotation of single bond and isomerism of imine ($\text{C}=\text{N}$).²⁰ The observation of fluorescence only in the solid state suggest the AIEE phenomena of 1-5.



Scheme 1. Molecular structures of 1-5.

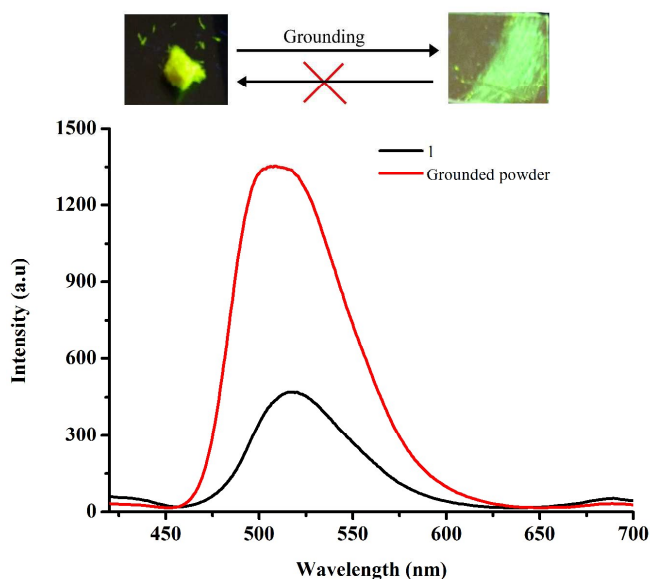


Fig. 1. Fluorescence tuning of 1 (digital images and fluorescence spectra) by hard grinding. $\lambda_{\text{exc}} = 365 \text{ nm}$.

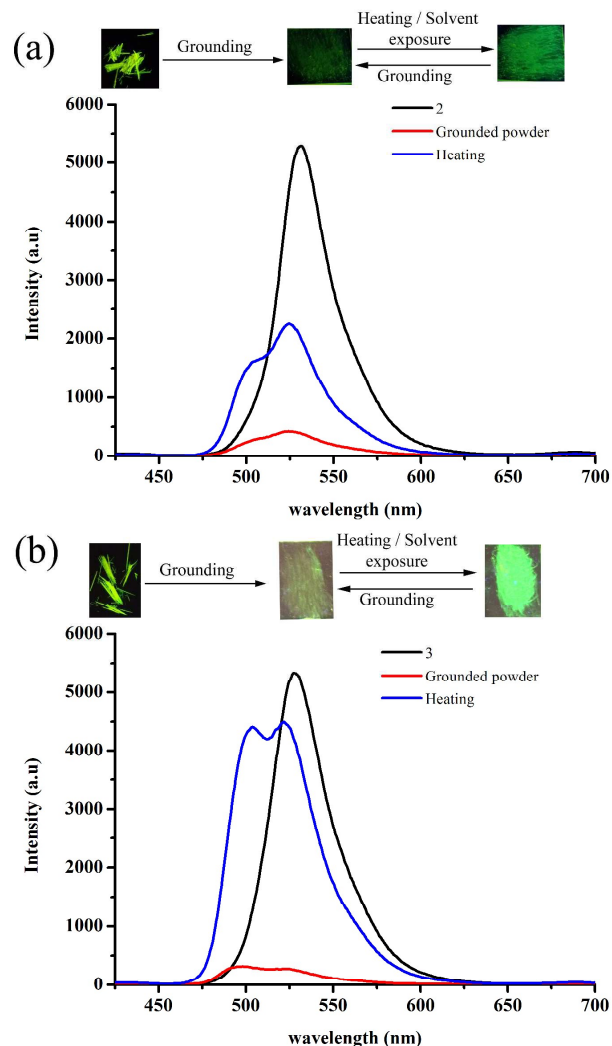


Fig. 2. Digital images and fluorescence spectra of off-on fluorescence switching of (a) 2 and (b) 3. $\lambda_{\text{exc}} = 365 \text{ nm}$.

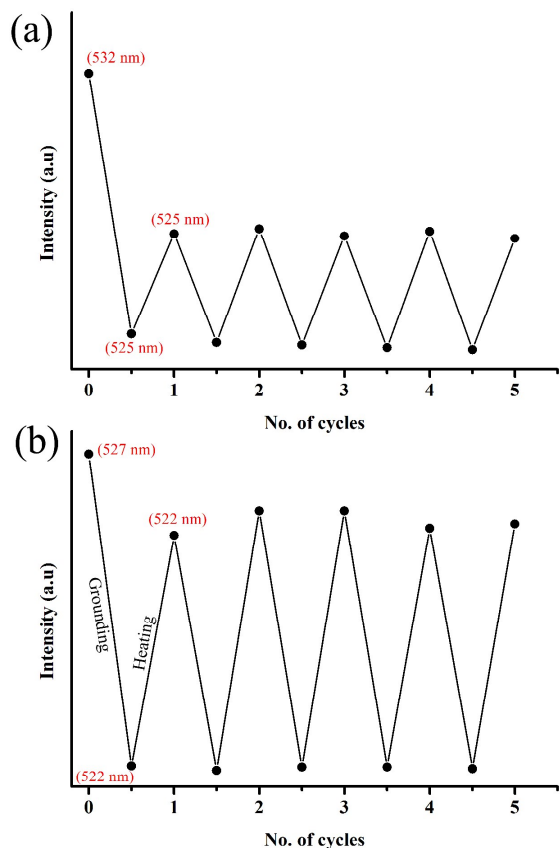


Fig. 3. External stimuli induced reversible off-on fluorescence switching between dark and bright state of (a) 2 and (b) 3.

1 showed greenish-yellow fluorescence with emission peak at 520 nm (Fig. 1, $\Phi_f = 40\%$). The strong grounding of 1 blue shifted the emission to 508 nm and showed green fluorescence ($\Phi_f = 43\%$). Heating or solvent vapor exposure did not show any fluorescence switching. The methoxy-salicylaldehyde group was replaced with naphthaldehyde in 2. The isomeric compound of 2 and 3 also showed greenish-yellow solid state fluorescence (Fig. 2). Fluorescence spectra of 2 and 3 showed emission at 532 and 527 nm, respectively ($\Phi_f = 46\%$ (2), 53% (3)). In contrast to 1, strong grounding of 2 and 3 exhibited quenching of fluorescence ($\Phi_f = 5\%$ (2), 7% (3)). The grounded powder showed only very weak fluorescence. Interestingly, the quenched fluorescence of 2 and 3 grounded powder was switched to bright green fluorescence upon heating or solvent vapor exposure. The digital images and fluorescence spectra confirmed the bright green fluorescence with enhanced intensity. It is noted that grounding and heating of 2 and 3 blue shifted fluorescence. 2 showed fluorescence at 525 nm along with a small hump at 500 nm after grounding and heating. Whereas 3 exhibited two clear fluorescence peaks at 503 and 522 nm after grounding and heating. The excitation spectra of 2 and 3 showed a small change after grounding and heating (Fig. S2 and S3). Importantly, 2 and 3 showed reversible fluorescence off-on switching (dark to bright fluorescence) without significant loss of intensity for more than five cycles by repeated grounding and heating (Fig. 3).

The carboxylic acid group was introduced at ortho position of 1 and 2 to further rigidifying the fluorophore in the solid state via intermolecular H-bonding interactions (4 and 5). 4 exhibited strong greenish-yellow fluorescence at 517 nm (Fig. 4a, $\Phi_f = 58\%$

%). However, strong grounding of 4 completely quenched the fluorescence ($\Phi_f = 10\%$). Heating/solvent exposure switched the fluorescence from dark to bright greenish yellow. The fluorescence spectra showed an enhanced fluorescence at 504 nm. The excitation spectra of 4 showed clear peaks at 370 and 492 nm (Fig. S4). The strong grounding showed the disappearance of peak at 370 nm and blue shift of 480 nm peak to 465 nm. Although heating did not show clear peak at 370 nm, the intensity has been clearly enhanced with slight red shift of 465 nm peak to 478 nm. This result supports the fluorescence change of 4 by hard grounding and heating. The fluorescence of 4 can also be repeatedly switched off-on for several cycles by hard grounding and heating (Fig. 4b). The as-synthesized powder of 5 showed strong yellow fluorescence at 536 nm (Fig. 5a, $\Phi_f = 48\%$). Surprisingly, the crystals of 5 showed only very weak fluorescence ($\Phi_f = 6\%$). However, slight breaking of crystals

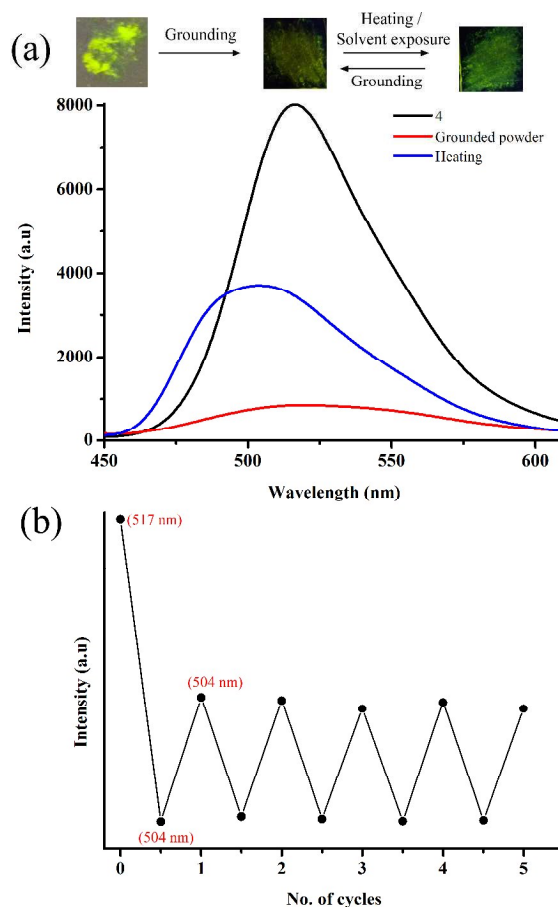
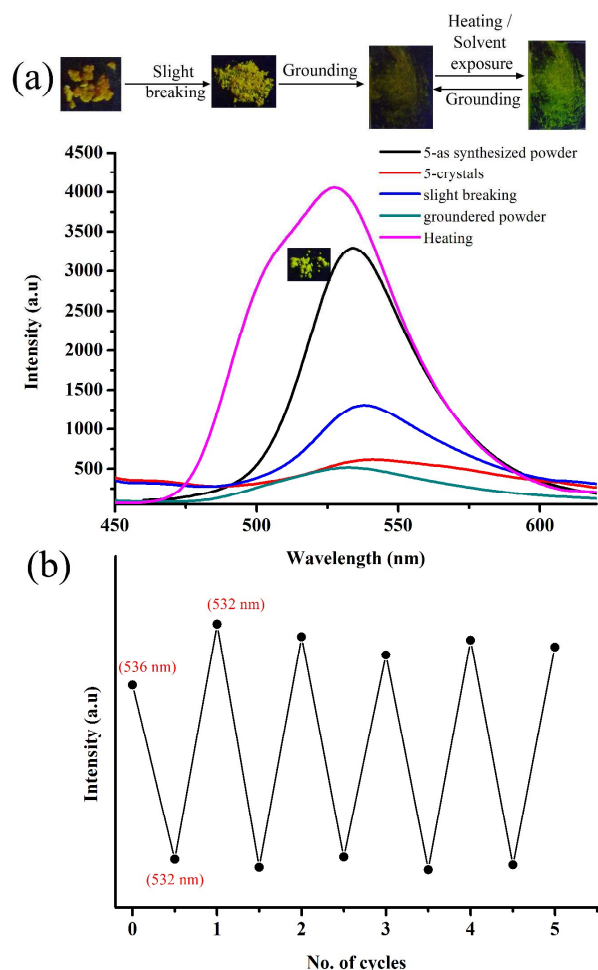


Fig. 4. (a) Digital images and fluorescence spectra of 4 and (b) external stimuli induced reversible fluorescence off-on switching. $\lambda_{exc} = 365$ nm.

lead to strong enhancement of fluorescence intensity ($\Phi_f = 34\%$). Similar to 2-4, hard grounding quenched the fluorescence intensity of 5 ($\Phi_f = 5\%$) and heating/solvent exposure produced bright greenish-yellow fluorescence. The strongly grounded powder showed very weak fluorescence and heating showed strong enhancement of intensity. The fluorescence λ_{max} was slightly blue shifted from 536 to 532 nm after grounding and heating. The excitation spectra of crystals and strongly grounded powder did not show any clear peak however, slightly broken

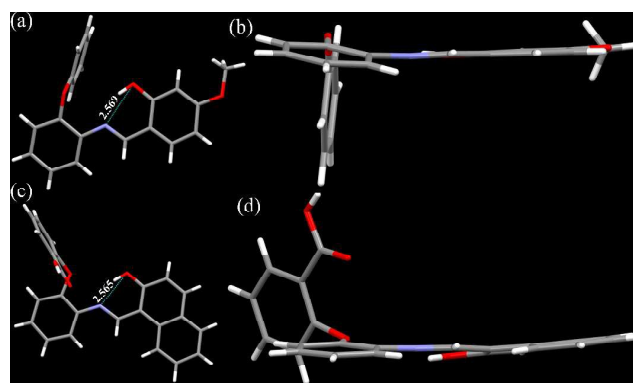
crystals and heated samples exhibited strong peaks with perfect matching (Fig. S5). The solid state fluorescence of 5 also exhibited repeated fluorescence off-on switching from dark to bright state for several cycles without significant loss of intensity by grounding and heating (Fig. 5b). Thus simple aryl-ether based Schiff base compounds (2-5) exhibited rare stimuli responsive fluorescence off-on switching and 1 showed fluorescence tuning. Importantly, 2-5 showed reversible dark and bright fluorescence switching with good contrast for several cycles.



10 Fig. 5. (a) Digital images and fluorescence spectra of 5 and (b) external stimuli induced reversible fluorescence off-on switching. $\lambda_{exc} = 365$ nm.

In an effort to understand the molecular arrangement and AIEE phenomena of 1-5 in the solid state, single crystals were attempted to grow from different solvents that includes methanol, ethanol, ethyl acetate, chloroform, dichloromethane, acetonitrile and acetone. 2 and 3 gave only thin plates from all solvents which did not show any X-ray diffraction. 4 formed more of amorphous powder with less crystalline phase. However, single crystals of 1 and 5 was obtained from methanol and dimethylsulfoxide, respectively (Table S1 and S2). 1 and 5 showed twisted molecular conformation in the crystal lattice (Fig. 6). The phenyl group of aryl ether adopted perpendicular orientation with respect to imine attached phenyl group in both 1 and 5. It is noted that the

25 conformationally flexible aryl-ether is known to adopt different conformation in the crystals including four different conformation in a single supramolecular structure.²¹ The imine and methoxy-salicylaldehyde are in same plane in 1 whereas naphthaldehyde in 5 is slightly twisted (Fig. 6b,d). The hydroxy group of 1 and 5 formed strong intramolecular H-bonding interactions with imine nitrogen in the crystal lattice (Fig. 7). Further, the strong intermolecular π - π interactions between imine phenyl group and methoxy phenyl group produced stair-like network structure in the crystal lattice (Fig. 7a). In 5, intermolecular H-bonding between hydroxyl groups lead to the formation of 1-D chains (Fig. 7b). Strong C-H...O (imine hydrogen and acid carbonyl oxygen) and π - π intermolecular interactions between the imine naphthyl groups lead to interdigitation of chains with face-to-face molecular arrangement of imine naphthyl groups (Fig. 7c). The face-to-face arrangement of imine naphthyl group might be the reason for fluorescence quenching in the crystals of 5 (Fig. 5a). The strong face to face π - π interactions are known to quench the solid state fluorescence of π -conjugated aromatic molecules.²² The slight breaking might have disturbed the face-face arrangement that turned on the fluorescence. Although, 1 also showed π - π interactions in the crystal lattice but it showed slip-stacking molecular arrangement between two different aromatic molecules. The structural studies of 1 and 5 clearly indicate the strong intra and intermolecular interactions in the crystal lattices. Thus, it is expected that 2-4 also could be having strong intermolecular interactions in the solid state due to structural similarity. These strong intermolecular interactions could restrict the free rotation and imine isomerism that induces AIEE in the solid state. The restriction of free rotation in Schiff base molecules by molecular design showed AIEE.²³



60 Fig. 6. Molecular conformation with intramolecular H-bonding interactions in the crystals lattice of (a, b) 1 and (c, d) 5. N (blue), O (red), H (white); H-bonds (broken line). H-bond distances are marked in Å.

The external stimuli induced switching or tuning of organic solid state fluorescence is generally due to the change of molecular conformation or phase (crystalline to amorphous).^{3,4} To gain the insight on the switching and tuning of 1-5 solid state fluorescence, PXRD measurements were performed before and

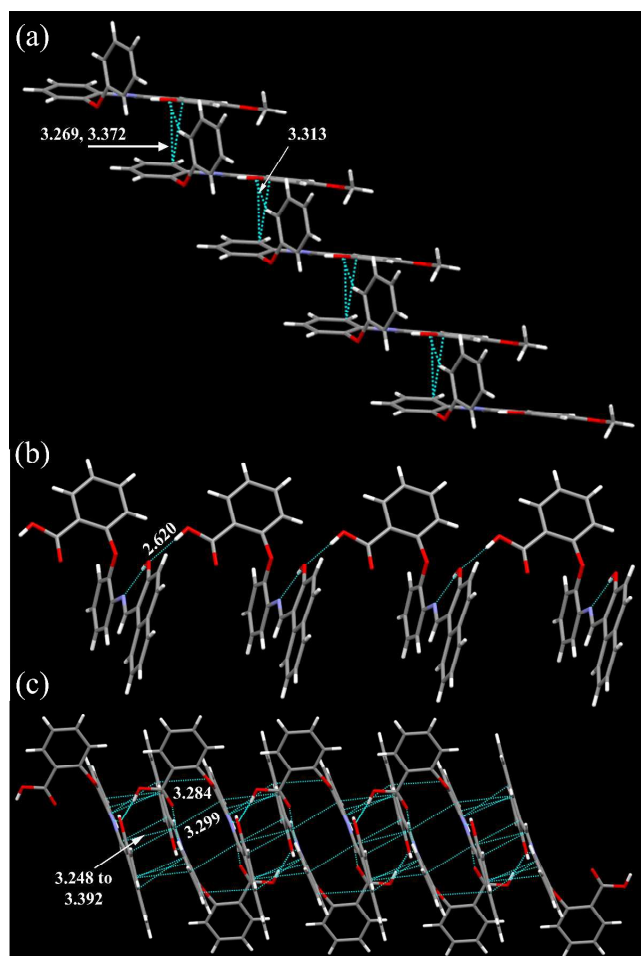


Fig. 7. (a) Stair-like network structure formation via π - π interactions in 1 and (b, c) linear chain and interdigitation chain via H-bonding and π - π interactions in 5. N (blue), O (red), H (white); H-bonds (broken line). H-bond and π - π interaction distances are marked in Å.

after applying the external force. The perfect matching of simulated and experimental diffraction pattern of 1 confirmed the phase purity of the sample (Fig. S6). The strong grounding of 1 modified the strong diffraction to weak diffraction peaks and suggests the formation of partial amorphous phase. The change of crystalline to amorphous phase of 1 blue shifted the fluorescence λ_{max} from 520 to 508 nm. 2 and 3 that formed thin needles showed clear diffraction peaks (Fig. 8a, S7). Strong grounding lead to the formation of amorphous phase, however, heating converted the amorphous to crystalline phase. PXRD studies of 4 that showed only weak diffraction peaks indicate the formation of more amorphous phase (Fig. S8). The weak diffraction peaks also disappear or reduced the intensity upon strong grounding and heating showed slight recovery of peaks. Similar to 1, the perfect matching of simulated and experimental pattern confirmed the phase purity of 5 (Fig. S9). The slight breaking of 5 produced more peaks and strong grounding lead to the formation of amorphous phase (Fig. 8b). Heating or solvent exposure converted the amorphous phase to crystalline phase. Thus PXRD studies indicate that switching off-on fluorescence of 2-5 and fluorescence tuning in 1 is due to the conversion of crystalline to amorphous phase with external stimuli. However, the reason for the fluorescence tuning in 1 and switching off-on in 2-5 by external stimuli is not clear. Single crystal studies of 5 showed

face to face molecular organization in the solid state that quenches the fluorescence. Hence it is speculated that strong grounding promotes face to face assembly in naphthaldehyde substituted compounds (2, 3 and 5) and might quenched the fluorescence. More structural studies are required to clearly understand the off-on fluorescence switching of Schiff base compounds which is currently under progress in our lab.

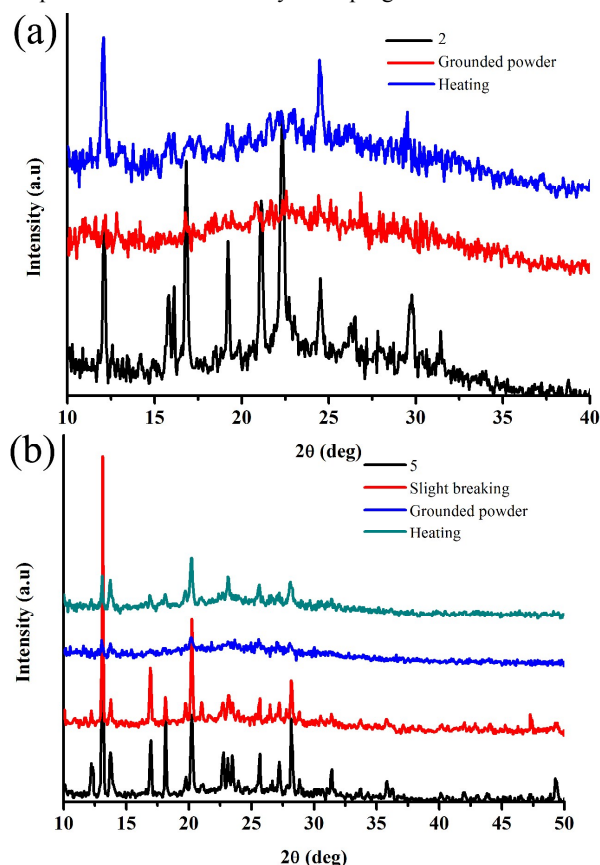


Fig. 8. PXRD pattern of (a) 2 and (b) 5.

Conclusion

In conclusion, we have demonstrated external stimuli dependent rare high contrast fluorescence off-on switching using simple aryl-ether amine based Schiff base molecules (1-5) that showed aggregation induced enhanced emission (AIEE) in the solid state. 1 showed irreversible fluorescence tuning from greenish-yellow to green upon hard grounding of solids. Heating or solvent exposure did not switch the fluorescence of 1. In contrast, strong grounding of 2-5 solids exhibited quenching of solid state fluorescence. Interestingly, heating/solvent exposure of strongly grounded powder (2-5) induced clear bright fluorescence. Importantly, reversible fluorescence off-on switching in 2-5 has been demonstrated for more than five cycles by repeated grounding and heating. PXRD studies suggest that the switching dark and bright fluorescence of 2-5 is due to the reversible change of crystalline to amorphous phase. Single crystal analysis of 1 and 5 confirmed the twisted molecular conformation and strong intermolecular interactions in the crystal lattice that would restrict the free rotation and rigidifies the fluorophores. Thus rare high contrast dark and bright fluorescence switching have been

realized using simple Schiff base molecules that could be of interest in optoelectronic device applications.

Acknowledgements

Financial supports from DST, New Delhi, India (DST Fast Track Scheme No. SR/FT/CS-03/2011 (G) and SR/FST/ETI-284/2011(c)) and CRF facility, SASTRA University are acknowledged with gratitude. AK and PSH thanks SASTRA University for research fellowship. "X-ray crystallography at the PLS-II 2D-SMC beamline was supported in part by MSIP and POSTECH. We thank Dr. C. R. Ramanathan for helping in NMR spectra.

Notes and references

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- † Electronic Supplementary Information (ESI) available: Electronic Supplementary Information (ESI) available: Absorption, fluorescence spectra, crystallographic table (1 (CCDC No. 1418264) and 5 (CCDC No. 1417738)).
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